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RESEARCH PAPER

Determination of Rare Earth Elements by ICP-MS in some Geological Samples in (Sulaimani) Kurdistan Region of Iraq.

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ABSTRACT:

Rare Earth Elements(REEs) were evaluated in three locations in sulaimani, Kurdistan region , five types of rock were selected (alkaline, peralkaline, mafic ,iron ore and intermediate rocks).Decomposition of the rock samples carried out by Lithium MetaBorate fusion ,the final sample solutions were prepared in 4% HNO_3.ICP-MS technique was selected for analysis of Rare Earth Elements in the rock sample ,results show presence of economic level of some Rare Earth Elements in Qaladza location (Bulfat mountain group),the high grade of Rare Earth Elements deposited in Nepheline synite.The best accuracy and precision were obtained by ICP-MS technique, the D.L for most Rare Earth Elements are between (0.01-0.3 ppm),with (0.999)of correlation coefficient , the solutions of the blank, standard solutions are monitored throughout the analysis and the analysis of duplicate also performed to obtain a good accuracy from our analysis.

KEY WORDS: Rare Earth Elements (REEs), ICP-MS, Nepheline synite, Igneous rocks.
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1.INTRODUCTION

Rare earth elements (*REEs*) are recognized as 17 elements with approximate physicochemical feature by the (IUPAC). Fifteen of the element from atomic number (Z=57 and Z=71) as follow lanthanum(La), cerium(Ce), praseodymium(Pr), neodymium(Nd),promethium(Pm),samarium(Sm), europium(Eu),gadolinium(Gd),terbium(Tb),dysprosium(Dy),holmium(Ho),erbium(Er),thulium(Tm) ,ytterbium(Yb) and lutetium(Lu).Scandium(Sc) Z=21) and yttrium((Y) Z=39) are somewhat apart from the lanthanide series(Ramos et al., 2016, Alonso et al., 2012).

Promethium(Pm) is not found *free* in nature and generally banned since all of its isotopes are radioactive with short half-live(Du and Graedel, 2013). *REEs* are regularly divided into light (LREE) and heavy (HREE) categories. The term (LREE) covers the La-Gd portion of lanthanide sequence (Z=57-64). Lanthanum characterized by filling up the 4f shell electrons, and one clockwise-spinning electron is added to each subsequent lanthanide until Gd heaviest of (LREE) is reached, the term (HREE) covers the Tb-Lu portion of the lanthanide sequence (Z=65-71) plus Y(Z=39) (Simandl, 2014). Depending on Environmental Protection Agency/ United States 2012, the abundance of *REEs* in the earth crust demonstrates that the lower atomic numbers of lanthanides are more abundant than one with higher atomic numbers as given in (Table 1). In technological applications, the character of the *REEs* and their geological distribution is quite comparable to each

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other (Chakhmouradian and Wall, 2012).The use of *REEs* have been found in a multitude electronic device, industry and medicine due to their unique electronic configurations so they are classified as “strategic critical metals”, *REEs* due to their ability of forming, alloyed with other metals, valuable and distinctive optical characteristics, including fluorescence and coherent light of emission, essential for laser device (Massari and Ruberti, 2013, Rojano et al., 2019).

For determination of *REEs* in real samples, several analytical methodologies have been applied such as; (INAA) Instrumental Neutron Activation Analysis(Aliyu et al., 2018), (XRF) X-Ray Fluorescence spectrometry(Schramm, 2016, Silva et al., 2020), (ICP-AES) Inductively Coupled Plasma Atomic Emission Spectrometry(Zybinsky et al., 2019), (ICP-OES) Inductively Coupled Plasma Optical Emission Spectrometry(Li et al., 2019), and (*ICP-MS*) Inductively Coupled Plasma Mass Spectrometry(Druzian et al., 2016, Gorbatenko and Revina, 2015, Zawisza et al., 2011). The most commonly used technique to analyse trace elements in geological samples is an(*ICP-MS*) a technique that incorporate multi-element capability, speed and high sensitivity(Li et al., 2017, Longerich et al., 1990). Even modern analytical technique as (*ICP-MS*) require pre concentration step, especially for elements like (Lu). A critical confirmation of analytical value must be carried out and quality control must be of the order of the day to assure the reliability of the data(El-Taher, 2010). Due to different type of sample, *ICP-MS* suffer from mass spectral interference such as isobaric, polyatomic ion and doubly charged ions, and from the influence matrix effect, as well as the variation in mass depends on the sensitivity of the instrument during analytical run, therefor all these effect can only be achieved by providing the fully quantitative measurement *ICP-MS* that minimized or corrected for, thus measurement will take place by selecting a compromise experimental condition, optimization of ion optic voltage, spiking sample with internal isotope (Lin et al., 2000).

The purpose of the present study is to validate the best target for ultra-trace *REE*-bearing mineral in five different types of rock as follows (alkaline, peralkaline, mafic, iron ore and intermediate rock) from sulaimani province, specially these present in economical level, and this performed by rapid and accurate analytical method like *ICP-MS* for different samples in different locations and zones.

Table(1). Estimated crustal abundance of *REE*s (Ganguli and Cook, 2018, Kumari et al., 2015, Long et al., 2012).

Elements	Atomic number	Estimate range (ppm)
Lanthanum	57	5-39
Cerium	58	20-70
Praseodymium	59	3.5-9.2
Neodymium	60	12-41.5
Promethium	61	10^{-18}
Samarium	62	4.5-8
Europium	63	0.14-2
Gadolinium	64	4-8
Terbium	65	0.65-2.5
Dysprosium	66	3-7.5
Holmium	67	0.7-1.7
Erbium	68	2.1-6.5
Thulium	69	0.2-1
Ytterbium	70	0.33-8
Lutetium	71	0.35-1.7
Yttrium	39	24-70

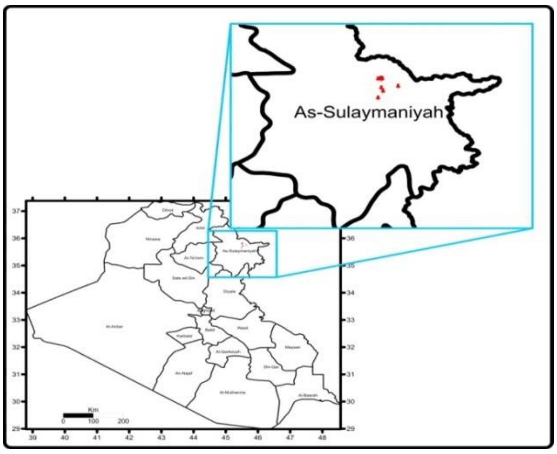

Figure (1): Map showing sampling sites.

2. MATERIALS AND METHODS

2.1 Apparatus

Analysis of *Rare earth elements*. Were done by ALS OMAC Laboratories Limited Ireland, using *ICP-MS* with the LMB Lithium MetaBorate fusion method ME-MS81 and MSA Labs Canada’s group, using method IMS-300, IMS-310, by using an *ICP-MS* perkin Elmer Nexion 300D was used for determination of *REEs* in rock samples. The optimum operating conditions for *ICP-MS* are summarized in (Table 2). Different parameters such as (RF power, plasma gas flow, auxiliary gas flow, and optimized the samples were injected through a peristaltic pump.

Table (2): Operating parameters for REE determination using ICP-MS.

RF Power	1500 W
Plasma gas	18 L/Min
Carrier gas	1.08 L/Min
Aux gas	1.2 L/Min
Peripump	4 Rpm
Data acquisition	Dwell time per AMU;50 ms
Reps	10 Sweeps /reading ,1 reading

2.2 Reagents and Reference Materials

The standard solution for the elements were prepared from following stock solutions; IV-*ICP-MS* 71A, Delta-STD-179 , IV-*ICP-MS*71B With solution matrix 4% HNO_3 , 0.7% LMB (Lithium Meta Borate).The concentration of *REEs* in the series of the standard solutions described in (Table 4).

Table (4): Including standard solutions for each element.

	Ce	Dy	Er	Eu	Gd	Ho	La	Lu	Nd	Pr	Sm	Tb	Tm	Y	Tb
10(ppb) Cal solution	1.90%	0.40%	1.00%	0.70%	1.50%	1.00%	1.30%	1.50%	1.50%	2.30%	1.80%	2.10%	1.90%	2.30%	2.20%
100(ppb)Cal solution	2.70%	1.80%	2.00%	4.40%	2.10%	1.50%	3.00%	2.10%	2.90%	3.60%	3.30%	4.30%	1.90%	3.40%	3.30%

2.3 sample collection

The study areas (**Fig.1**) were chosen on the basis of *igneous rock* (granitoid pegmatite, granite, *Nephelen Syanite* , basalt, gabbro, diorite **,** chromitite and magnetite) referring the geological map of sulaimani region. In this study we have selected three areas of different climates with the help of geology department /college of science e.g. (MOC) Mawat ophiolite complex (11samples), (POC) Penjwen Ophiolite complex (4 samples), the (BMG) Bulfat Mountain Group/Qaladze city (6 samples), as summarized in(Table 3).

Table (3): Including some description about these rocks.

Sample NO.	**Rock type**	**Location**	**description**
MO1	basalt	MOC	is a mafic volcanic *igneous rock*, dark or black in color(Lapena and Marinucci, 2018).
MO2	gabbro	MOC	mafic plutonic coarse -grained *igneous rocks* compose equally to basalts, basalt , represent as a magma that has

			crystallized slowly at depth(Gill, 2010).
MO3,MO4	diorite	MOC	Is intermediate, between that of mafic gabbro and felsic granite. dark gray, holocrystalline, with fine grained (1—2 mm) equigranular texture and compact block structure(Li et al., 2005).
MO6,MO7,MO8, MO9,MO10,MO 11	Granitoid pegmatite	MOC	Pegmatites are plutonic felsic *igneous rocks* with very coarse-to gigantic-sized textures. It is a combination of gigantic crystal size and extreme enrichment of rare elements, Which symbolises the world’s most famous granitic pegmatites(Simmons, 2007). Although pegmatites were the first bedrock source of REEs exploited in the first half of the 1900s to meet an

			increasing demand for Ce, Y(Chakhmouradian and Zaitsev, 2012) .
MO5	chromite	MOC	chromite occurs exclusively in mafic and ultramafic igneous rocks(Koleli and Demir, 2016). it is chromium mixed with iron oxide, with vary amounts of magnesium and aluminium, the general formula being $(Fe,Mg)O.(Cr,AI,Fe)_{2}0_{3}$(Gu and Wills, 1988).
PO14,PO15	magnetite	POC	Magnetite or ferrous ferrite (FeO, Fe2O3 or Fe3O4) is an iron oxide(iron ore) which has an inverse spinel structure with Fe(III) ions distributed randomly between octahedral and tetrahedral sites, and Fe(II) ions in octahedral site(Sulistyaningsih et al., 2017).
PO12,PO13	granite	POC	Granite is a common type of felsic intrusive *igneous rock* consisting of quartz, feldspars,

			and micas which is granular and phaneritic in texture. Granites can be predominantly white, pink, or gray in color, depending on their mineralogy(Johannes, 1996).
BG16,BG17,BG18, BG19,BG20,BG21	*Nepheline syenite*	BMG	is a light-colored alkaline *igneous rock* formed mainly of alkali feldspar and *nepheline* in appreciable amounts. It is similar in appearance to coarse-grained granite but characterized by absence of quartz(Abouzeid and Negm, 2014).

2.4. Procedure

2.4.1. Lithium MetaBorate Fusion (LMB)

0.15g of a powder sample and 0.7 % of LMB were placed in a platinum crucible at 1000 C^o for 1 hour in muffle furnace. The residue was leached from the cooled crucible by an additional 4% HNO_3 solution. The solution obtained was transferred to a volumetric flask and then diluted to a final volume of 100 ml with distilled water.

3. RESULTS AND DISCUSSIONS

Three sets of igneous rocks were used for preparation of sample solutions, which expected to contain different amount of *REEs*, the focal point to this study for these rocks which contain economic grade of lanthanide. *REEs* occur naturally in diversity of mineral type. LREE are found in bastansite, monazite, ancylite, lanthanite, stillwellite, allanite, cerianite, britholite and laporite, while HREE and Y(yttrium) are mostly associated with minerals such as xenotime, yttrotantalite, euxenite, samarskite and gadolinite(Khan et al., 2017). Above all, *Rare Earth Elements* resources are distributed among many mineral deposits, but only a portion will be economic to develop and mine. Only quite abundant deposits can be called reserve of rare earth, but that amount cannot be reliable practically and economically. Generally *ICP-MS* technique is the best for determination of trace contents of *REEs* in the rock sample due to its good sensitivity and selectivity(Li et al., 2017, Longerich et al., 1990). As shown from results the D.L for most *REEs* by this technique is between (0.01-0.3ppm), the correlation coefficient R-squire

(0.999-0.9999) after calibrations, aqueous quality control solutions are analysed at regular intervals throughout the run to achieve best sensitivity for results. To obtain good selectivity an internal standard method also used to correct for drift, c(Chakhmouradian and Wall, 2012) correlation factor and alternate masses are used for correct spectral interference, digested blanks, certified reference materials and duplicates are monitored also throughout the analysis.

According to crustal abundance of individual *REEs* that indicate in (Table 1), some type of different samples in (Table 5) are from Mawat Ophiolite (MO),as follows; the mafic rock e.g.(MO1, MO2) and intermediate rock e.g.(MO3 , MO4), these types in which mentioned above carried minimum amount of *REEs* deposit. However granitic pegmatite in e.g. (MO6, MO7 until MO11) which contain relative concentration of (Ce) specially in MO6, so we cannot interdependent of the Mawat pegmatite for determining economic grade of *REEs* . Particular content of the *REEs* in (MO6) are not desirable for description.

In (Table 6) in which four cases collected in Asnawa deposit from Penjwen district each of this type e.g.(PO12 and PO13) is a granite rock, peralkaline granites carry relative grade of *REEs* in addition allanite and monazite. Which are typical LREE hosts in most granitoid, peralkaline varieties contain HREE and Y minerals as xenotime. Iron ore in magnitite rock mineral e.g. (PO14 and PO15) in which Fe-ore relative enrichment of REE-bearing mineral.

The results that are given in (Table 7) are the *Rare Earth Elements* distribution in six selected main rare-earth deposit from Bulfat Mountain in Qaladze city. The concentration of LREE and HREE ploted across the *Nepheline syenite* zones (Figure 2 and 3) the bulfat *Nepheline syenit*e show uniform distribution pattern of LREE and HREE, with LREE being more enriched relative to HREE. The relatively high concentration of LREE in *Nepheline synite* in Bulfta group may be related to occurrence of Monazite at the border zone. The summation of LREE and HREE concentration pattern show gradual decreasing toward the core of the *Nepheline* bodies. Moreover, the relation between LREE and HREE in different zone are variable with the LREE been more enriched as compared to HREE in the border zone with inverse relation toward the core zone (Figure 4).

Table (5): Certified and consensus values of *REEs* in (11) different samples in Mawat Ophiolite Complex.

Sample location	Mawat Ophiolite Complex											
Sample No.	**MO1**	**MO2**	**MO3**	**MO4**	**MO5**	**MO6**	**MO7**	**MO8**	**MO9**	**MO10**	**MO11**	**D.L**
REE(ppm)												
La	0.6	0.4	0.3	0.8	1.8	13.4	2.4	3.5	1.7	1.3	0.5	0.5
Ce	0.6	0.4	0.3	2.2	2.9	30.8	14.4	11.3	7.5	5.6	2	0.5
Pr	0.21	0.07	0.09	0.35	0.56	0.39	2.87	1.51	1.25	0.88	0.34	0.03
Nd	1	0.3	0.5	2.4	1.8	15.6	13.3	5.2	5	3.6	1.6	0.1
Sm	0.42	0.31	0.41	1.31	0.56	3.36	5.92	1.61	1.8	1.61	0.88	0.03
Eu	0.17	<0.03	0.14	0.93	0.44	0.9	0.05	<0.03	<0.03	<0.03	<0.03	0.03

Gd	0.71	0.11	0.58	1.35	1.01	3.39	0.86	1.19	1.11	1.2	0.57	0.05
Tb	0.1	0.03	0.08	0.25	0.19	0.55	0.05	0.21	0.2	0.26	0.11	0.01
Dy	0.94	0.5	0.93	1.59	1.31	3.42	0.55	1.1	1	1.45	0.51	0.05
Ho	0.21	0.05	0.15	0.4	0.35	0.66	0.3	0.17	0.17	0.24	0.1	0.01
Er	1.05	0.23	0.62	1.6	1.01	1.98	0.21	0.52	0.51	0.73	0.3	0.03
Tm	0.17	0.01	0.07	0.14	0.14	0.31	0.05	0.1	0.09	0.14	0.07	0.01
Yb	0.71	0.06	0.69	0.19	1.15	2.13	0.22	0.63	0.62	1.07	0.35	0.03
Lu	0.12	<0.03	0.1	0.18	0.15	0.37	0.01	0.09	0.1	0.17	0.05	0.01
Y	7.1	1.7	5.8	13.8	8.1	16.3	2	5.5	5.5	8.3	3.3	0.5
Σ REE	14.11	4.17	10.76	28.49	21.32	93.56	43.19	32.63	25.55	26.15	10.68	
Total LREE	3.71	1.59	2.32	9.34	8.92	67.84	39.8	24.31	18.36	13.79	5.89	
Total HREE	10.4	2.58	8.44	19.15	12.4	25.72	3.39	8.32	8.19	12.6	4.79	

Table (6): Certified and consensus values of *REEs* in (4) different samples in Penjwen Ophiolite Complex.

Sample location	Penjwen Opheolite Complex				
Sample No.	**PO12**	**PO13**	**PO14**	**PO15**	**D.L**
REE (ppm)					
La	54.5	13.2	17	4.5	0.5
Ce	74.8	18.9	25.3	12.8	0.5
Pr	8.56	2.35	4.11	2.01	0.03
Nd	30.2	10.1	14.3	10.4	0.1
Sm	5.56	3.8	4.08	3.27	0.03
Eu	2.2	1.83	0.82	1.51	0.03

Gd	5.18	3.9	4.01	3.9	0.05
Tb	0.77	0.7	0.63	0.77	0.01
Dy	4.2	3.91	3.29	4.76	0.05
Ho	0.82	0.79	0.71	1.01	0.01
Er	2.41	2.13	1.86	2.87	0.03
Tm	0.36	0.33	0.33	0.41	0.01
Yb	2.1	1.89	1.67	2.49	0.03
Lu	0.33	0.3	0.24	0.38	0.01
Y	21.9	21	20.3	25.1	0.5
Σ REE	213.89	85.13	98.65	76.18	
Total LREE	181	54.08	69.62	38.39	
Total HREE	32.89	31.05	29.03	37.79	

Table (7): Certified and consensus values of *REEs* in (6) different sample in Bulfat Mountain Group.

Sample Location	Bulfat Mountain Group						
Sample No.	**BG16**	**BG17**	**BG18**	**BG19**	**BG20**	**BG21**	**D.L**
REE(ppm)							
La	39	14.2	15.9	8.2	0.3	0.8	0.5
Ce	72.6	31.8	33.8	16	0.5	1.6	0.5
Pr	8.2	4.01	4.1	1.89	0.05	0.21	0.03
Nd	30.3	16	16.2	7.2	0.2	0.8	0.1
Sm	5.38	3.51	3.29	1.5	0.08	0.21	0.03
Eu	1.8	1.06	0.89	0.75	0.03	0.07	0.03
Gd	4.76	3.48	3.33	1.46	0.07	0.2	0.05

Tb	0.71	0.6	0.56	0.26	0.01	0.04	0.01
Dy	3.87	3.60	3.33	1.67	0.08	0.22	0.05
Ho	0.75	0.82	0.7	0.35	0.02	0.07	0.01
Er	2.25	2.41	1.98	1.17	0.05	0.31	0.03
Tm	0.34	0.36	0.28	0.2	0.02	0.11	0.01
Yb	2.22	2.1	1.74	1.21	0.07	1.25	0.03
Lu	0.37	0.33	0.28	0.22	<0.01	0.35	0.01
Y	19	21.9	17.8	9.4	0.5	1.7	0.5
Σ REE	192.74	106.18	104.18	51.48	1.98	7.94	
Total LREE	162.04	74.06	77.51	37	1.23	3.89	
Total HREE	30.7	32.12	26.67	14.48	0.75	4.05	

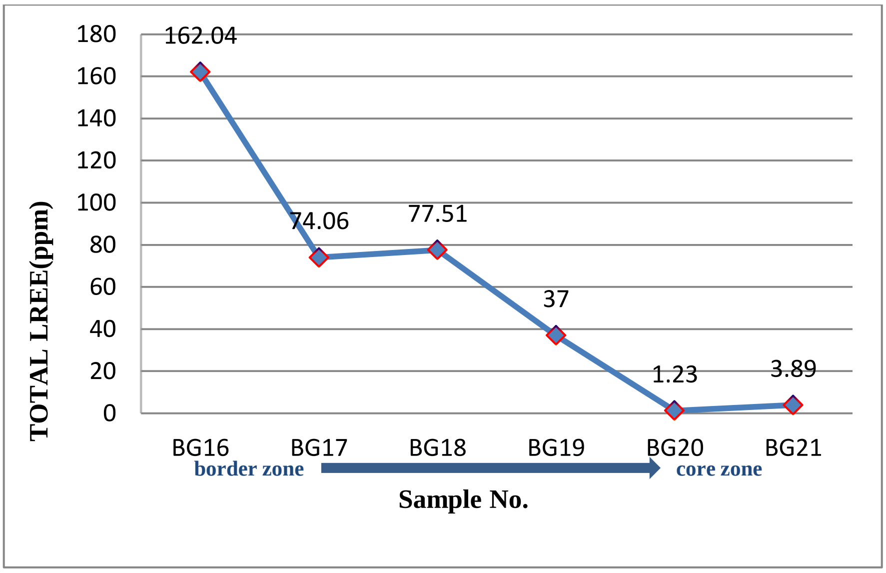

Figure (2): Total (LREE) pattern across the bulfat *Nepheline syenite* zones.

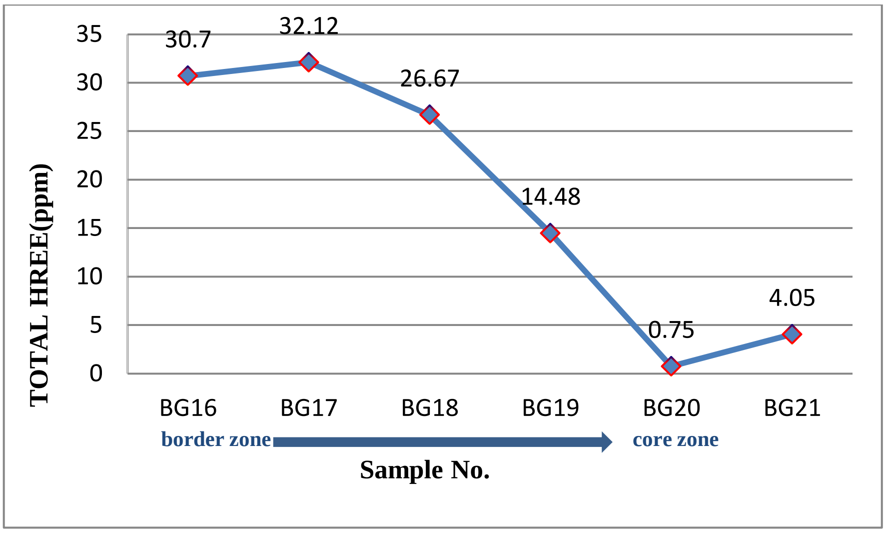

Figure (3): Total (HREE) pattern across the Bulfat *Nepheline syenite* zones.

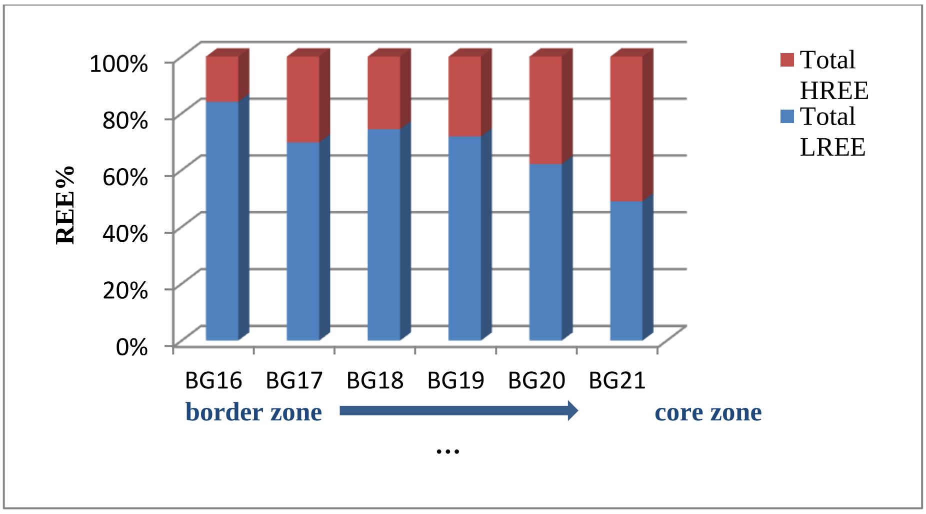

Figure (4): Relationship between (LREE) and (HREE) in deferent zones Bulfat *Nepheline syenite* zones.

4. CONCLUSIONS

Accurate and reproducible method was reported for determination of *REEs* in some geological samples, by dissolution of powder sample with the aid of LMB and measurement with ICP-MS technique. This protocol applied to twenty one *igneous rock*, based on the analytical data of three groups of *igneous rock* sample in Sulimani province (MOC-POC and BMG) of variable rock type including (Basalt, Gabbro, diorite, Chromite, Granoited Pegmatite, Granite, Magnetite, and in *Nepheline synite*), for future the best candidate for *REEs* in which more economic and valuable deposits for exploration and extraction is in *Nepheline synite* from Bulfate group, the high concentration of *REEs* in this type of rock is probably related to occurrence of *REE* bearing mineral monazite.

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